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Stabilization of Casein Fibers by Desamination*

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Abstract

Casein fibers hardened with formaldehyde solutions need further processing to withstand boiling acid dye baths. Studies on desamination of casein fiber at various steps in the spinning process are reported. Desamination of casein fiber increases its resistance to dye baths. Desaminated fiber is given additional stability by treatment with acid-formaldehyde solutions followed by baking at 110°C. Dye uptake of both acidic and basic dyes is reduced by the combined treatment.

PREVIOUS PAPERS from this laboratory have reported studies designed to increase the strength of casein fibers [11] and to develop continuous-filament yarns by pot spinning [12]. Stabilizing casein fibers hardened with formaldehyde so that they can be treated with boiling aqueous acid dye baths without shrinkage or loss of tenacity is a formidable problem, but it must be considered an essential part of fiber production.

Acetylation was used to stabilize the commercial casein fiber Aralac [2]. Papers from this laboratory [3, 12] gave experimental data on the acetylation process for our casein fiber, but pointed out the deficiencies of the process. Because acetylation must be effected under almost anhydrous conditions, the process requires careful control. Also, the use of a flammable hydrocarbon solvent as a diluent for the acetic anhydride makes the process a serious fire hazard. A process in which only aqueous solutions are used for stabilizing casein fibers would obviate this fire risk. A treatment with acid-formaldehyde solutions followed by drying and baking has given moderate stabilization [13], but increasing the stabilization of tensile strengths from 80% to nearly 100% is difficult.

Desamination of casein has been the subject of many reports in the literature [1, 6, 7, 16]. However, because little quantitative information is given, this investigation was undertaken to determine to what extent desamination might be carried and the maximum stability to be obtained from the process.

Apparatus and Methods

The casein fiber used in this work was in the form of a 300-den. 40-filament yarn with about 3 turns Z-twist per in. Its preparation and testing for tenacity have been described elsewhere [12].

To evaluate the resistance to boiling baths used in applying acid dyestuffs, a standard procedure was developed. Two g. of yarn were tied in a loose hank and boiled under reflux for 1 hr. in 80 ml. of solution containing sufficient acetic acid to give pH 4 and 10% sodium sulfate (based on the weight of the fiber). The fiber was rinsed, centrifuged in a small basket centrifuge, and dried at 100°F. Then it was conditioned for at least 2 hrs. before being tested at 50% relative humidity and 73°F. The tenacity obtained after simulated dyeing in this fashion is referred to as "tenacity after boiling."

Equilibrium dye uptake was determined by the method of Fraenkel-Conrat and Cooper [5]. The samples of fiber were ground in a Wiley mill and shaken with the dyes and buffer for 24 hrs. at 73°F in a constant-temperature room. Cross sections were made of fiber dyed in a similar manner, but not ground in the Wiley mill. The fibers did not show ring dyeing, and were uniformly stained across the section.

Reflectances were measured on a fabric knit from the dyed yarn on a 300-needle half-hose knitting machine. The fabric was doubled and redoubled; then the reflectance curve was run on a General Electric

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TABLE I. Effect of Temperature of "Blank" Dye Bath on Tenacity and Shrinkage of Fiber

Temperature of dye bath (°C)	Tenacity after dyeing (g./den.)	Loss in tenacity (%)	Denier	Shrinkage in length (%)
Control	1.06	—	275	—
40	1.03	0	305	9.5
50	1.06	0	298	8.0
60	1.00	6	306	10.0
70	0.88	18	340	19.0
80	0.65	39	402	32.0
90	0.63	41	428	36.0
100	0.11	90	519	47.0

recording spectrophotometer. A wave length of 440 mμ was chosen; here the reflectance curve showed the greatest difference for treatment with increasing amounts of nitrous acid. The colors ranged from light yellow to deep orange.

Van Slyke amino nitrogen determinations were made on the solid fiber by the method of Doherty and Ogg [4]. The fibers were ground to pass 60-mesh sieves in the Wiley mill.

Experimental Procedure

To show the effect of temperature in accelerating the loss of formaldehyde from the yarn before it is stabilized, 2-g. samples of the yarn were held in the blank dye bath for 1 hr., but at temperatures increasing from 40°C to the boil. The values for shrinkage in length and loss in tenacity, shown in Table I, reflect the loss of formaldehyde. Rath, Essig, and Abele [14] showed that the formaldehyde driven off in 1 hr. rose from 5% at 60°C to 70% at 100°C.

Desamination can be effected at several stages in the spinning process. Casein can be desaminated by sodium nitrite or nitrous acid before preparation of the spinning solution. If the desaminated casein is not allowed to dry out before it is dissolved in dilute alkali, a solution suitable for spinning can be made. The properties of the resulting fiber are disappointing, however, as the tenacities of both the wet and the dry fibers are lower than those of untreated casein. This result is not unexpected, because selective benzoylation of the amino groups of the casein before spinning, by the method of Mellon, Korn, and Hoover [8], also gives a fiber of low tensile strength. The present spinning method is based on partial hardening with formaldehyde, stretching, and then complete hardening. Covering the amino groups or removing them interferes with the hardening process, and, as a result, less tension can be applied to the tow before it breaks. Stretching is necessary to give greater tenacity [11].

TABLE II. Effect of Sodium Nitrite in Final Wash Bath at pH 6 on Stability of Fiber

Final wash	Tenacity of dry fiber (g./den.)	Tenacity of wet fiber (g./den.)	Tenacity of boiled fiber (g./den.)	Loss of tenacity on boiling (%)
30% Acetate (Control)	1.20	0.34	0.06	95
30% Acetate plus 5% sodium nitrite	1.14	0.33	0.28	75

TABLE III. Effect of Increasing Ratio of Nitrous Acid to Amino Groups on Stability of Fiber (Treatment at 25°C for 2 Hrs.)

Ratio of HNO_2/NH_2	Tenacity at 73°F, 50% R.H. After treatment (g./den.)	After boiling (g./den.)	Loss in tenacity (%)	Color
Control	1.12	0.14	88	White
3.33×	0.97	0.59	39	Light yellow
6.66×	1.03	0.61	41	Light yellow
10.0×	1.04	0.64	38	Yellow
13.3×	1.04	0.65	37	Yellow
16.6×	1.04	0.69	34	Orange
33.3×	1.01	0.69	32	Orange
33.3×(16 hrs.)	1.11	0.83	25	Brownish orange

Nitrous acid can be applied in the acid precipitating bath, the stretching bath, or the wash bath used to adjust the pH of the fiber before it enters the pot, but many experiments have shown that only in the last bath can nitrous acid be used without seriously affecting the tensile strength. Comparison with control yarns (Table II) shows that a small improvement in boil-resistance results from this treatment.

After the raw fiber has been further hardened so that it contains 2% formaldehyde, stronger nitrous acid solutions can be applied without affecting the tensile strength. The improvement in boil-resistance caused by the increased desamination is considerable. The nitrous acid, formed by reaction of equivalent quantities of acetic acid and sodium nitrite, is used in excess, based on 0.8% free amino nitrogen in casein. The fiber is treated in a batch process, in which a bath-to-yarn ratio of 30 to 1 is employed. Table III shows that the loss in tenacity on boiling may be cut from 88% to 25% but that the fiber is deeply colored.

Additional quantitative information is needed to show the other effects of nitrous acid on the yarn.

TABLE IV. EFFECT OF INCREASING RATIO OF NITROUS ACID TO AMINO GROUPS ON PROPERTIES OF YARN AND FABRIC (TREATMENT AT 25°C FOR 2 HRS.)

Ratio of HNO_2/NH_2	Dye uptake at pH 2.2 (equiv. dye per 10^4 g. fiber)	Amino nitrogen (%)	Reflectance of fabric at 440 mμ (%)
Untreated	5.3	0.75	63
3.33×	4.1	0.24	31
10.0×	2.5	0.16	13
33.3×	1.8	0.10	9
33.3×(16 hrs.)	1.5	0.05	—

TABLE V. STABILIZATION OF DRY FIBER CONTAINING 2% FORMALDEHYDE BY BAKING IN ACID CONDITION (110°C FOR 30 MIN.)

Impregnating solution	Tenacity of dry fiber at 73°F, 50% R.H. After baking (g./den.)	After boil test (reconditioned) (g./den.)
1% HCl—10% CH_2O	1.08	0.61
2% HCl—10% CH_2O	1.05	0.69
3% HCl—10% CH_2O	1.11	0.70
5% HCl—10% CH_2O	1.08	0.68
None (control)	1.20	0.06

Dye absorption at equilibrium with an acid dye in excess is used as a measure of the relative numbers of basic sites available. The content of Van Slyke amino nitrogen is a measure of the unreacted amino groups left in the yarn which will react with the relatively more-concentrated HNO_2 in the reaction chamber. The increasing depth of color of the fiber is a considerable drawback, because it must be reduced by bleaching with dithionites, for example, before the fiber can be dyed with light shades. These qualities are summarized in Table IV.

The reduction in dye uptake parallels the decrease in Van Slyke amino nitrogen, but the change in amino nitrogen content is greater than that in acid dye uptake, for the latter reaction is related to the sum of all the basic groups present. The absorption of a basic dye, Safranine O, was not increased by desamination, as had been reported for wool [15].

TABLE VI. FURTHER STABILIZATION OF CONTINUOUS-PROCESS DESAMINATED YARN BY BAKING IN ACID CONDITION (110°C FOR 30 MIN.)

Impregnating solution	Tenacity of dry fiber at 73°F, 50% R.H. After baking (g./den.)	After boil test (reconditioned) (g./den.)
1% HCl—10% CH_2O	1.02	0.78
2% HCl—10% CH_2O	0.99	0.89
3% HCl—10% CH_2O	1.04	0.84
5% HCl—10% CH_2O	0.99	0.81
Control (desaminated)	1.14	0.28

TABLE VII. BOIL-RESISTANCE AND REFLECTANCE OF FIBER STABILIZED BY FORMALDEHYDE, BAKING, AND DESAMINATION (2.3 RATIO, 25°C, FOR 2 HRS.) AND SUBSEQUENTLY BLEACHED VERSUS THOSE OF ACETYLATED FIBER

Tenacity at 73°F, 50% R.H. Original fiber (g./den.)	Treated and bleached fiber (g./den.)	Boiled fiber (g./den.)	Reflectance of boiled fiber at 440 mμ (%)
1.1	1.1	0.86	43
1.2	1.0	0.80	48
1.0	1.0	0.90	48
	Acetylated	Acetylated	
1.2	0.94	0.61	—

Previously reported work [13] has shown that treatment of finished fiber containing 2% formaldehyde in an acid-formaldehyde solution, followed by drying at increasing temperatures, produces a moderate degree of stability to boiling in acid dye baths. As shown in Table V, for the type of fibers used in this work, the acid strength could be varied from 2% to 5% without changing the strength of the treated fiber, but additional increase in acid concentration lowered the strength after treatment and the boil-resistance.

The advantage of this method over desamination lies in the resulting color of the product. If sulfuric acid is used instead of hydrochloric acid, a lighter color is obtained, but the fiber must be baked at a slightly higher temperature to obtain the same degree of stabilization. It remained to be proved whether the two stabilization processes were additive, or whether one would cancel the effect of the other. The yarn described in Table II, which showed about 0.16% amino nitrogen by the Van Slyke determination, was given the acid baking treatment, and the amount of acid was varied within the same limits as before. Table VI shows the improvement in boil-resistance.

The residual color may easily be removed by dithionite, as the acid-formaldehyde solution seems to have some bleaching action of its own. The loss of tenacity of the stabilized and bleached yarn when boiled is only 10%. The combined process represents an improvement over the acid baking process, and the color imparted to the yarn is less than that

TABLE VIII. MODIFICATION OF PROPERTIES OF YARN BY COMBINING CHEMICAL TREATMENTS

Treatment	Tenacity at 70°F, 50% R.H. (g./den.)	Tenacity of wet fiber (g./den.)	Amino N (%)	Acid dye absorption (equiv. dye per 10^4 g. fiber)	Basic dye absorption (equiv. dye per 10^4 g. fiber)	Water absorption† (%)
None	1.21	0.40	0.8	4.95	12.1	33.0
Desaminated*	1.10	0.49	0.05	1.85	11.2	30.4
Acid-CH_2O + baking at 110°C	0.96	0.31	0.15	4.1	5.65	31.0
Combined treatments	1.11	0.51	0.09	1.80	5.55	28.8
Acetylated	0.94	0.31	0.09	1.95	12.8	36.5

* 16 hrs. at 25°C, 33.3/1 ratio HNO_2/NH_2.
† Imbibed water not removed by centrifuging for 5 minutes at 1,000 relative centrifugal force.

shown in Table IV for the treatment in which the yarn after hardening was desaminated to 0.24% amino nitrogen.

Desamination can also be carried out as a batch process before the fiber is stabilized by acid baking with formaldehyde, as previously reported [13]. Table VII shows tenacity and reflectance measurements of 3 typical samples. Even after boiling, the fiber had a tenacity of 0.8 to 0.9 g. per den., and its reflectance of 48% can be compared with the value of 63% for the untreated fiber. Acetylation of these 40-filament yarns gives less effective stabilization than acetylation of the 150-filament yarns previously reported [12].

Table VIII contains comparison of the other effects of the stabilization process. Tenacity of the wet fiber was improved by intensive desamination. The color produced by this desamination could not be fully bleached. Dye absorption for both acid and basic dyes was decreased by the combined process. The tenacity of the colored yarns was stabilized at as much as 0.96 g. per den. after boiling. Water absorption was decreased by desamination and acid baking. Surprisingly, in contrast to results reported for earlier work [3], acetylation in a solvent increased the water absorption. A different method of acetylation was used [12] to avoid excessive loss of tenacity. Even under these conditions, acetylation may remove 0.5% formaldehyde.

Discussion

When nitrous acid reacts with casein, the ϵ-amino groups of lysine are rapidly converted to ϵ-hydroxy groups. The arginine, tyrosine, and tryptophane contents also enter into the reaction. The reaction with tyrosine is probably responsible for the color produced by desamination, because nitroso derivatives of tyrosine have been demonstrated [9].

The effect of desamination in increasing the strength of the wet fiber and its stability to boiling is best explained by the addition of new cross bonds. The stress-strain curve for the wet fiber shows a definite yield point, as compared with that of the unmodified fiber. The bonds are probably diazo linkages [10]. Additional support is given to this theory by the fact that when fibers stabilized by desamination are reduced with dithionite to remove the color, their strength after boiling is decreased slightly by this treatment.

The nature of the chemical reactions produced by baking after acid and formaldehyde treatment has not been demonstrated. The reduction in basic-dye binding capacity indicates that Koch's suggested mechanism of carboxyl group esterification with methylene glycol might be partially correct [7]. In addition, the reduction in acid-dye absorption follows the decrease in Van Slyke amino nitrogen. It is probable that these acid-resistant cross bonds involve some of the amino nitrogens in the fiber.*

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* NOTE: The mention of any specific equipment in this paper does not imply that these products are endorsed or recommended by the U. S. Department of Agriculture over others not mentioned.

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